Rec'd PCT/PTO 28 APR 2005



**PCT** 

REC'D 1 1 MAR 2005

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

	cant's c		nt's file reference	FOR FURTHER ACTIO	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. International filing date (de PCT/GB 03/04665 30.10.2003				International filing date (day/n 30.10.2003	month/year) Priority date (day/month/year) 04.11.2002
	national C30/0		nt Classification (IPC) or	both national classification and IP	PC
Appli DOI		TER	S LIMITED et al.		
1.	This Autho	interr ority a	ational preliminary ex and is transmitted to th	amination report has been pre le applicant according to Artic	repared by this International Preliminary Examining cle 36.
2.	This	REP	ORT consists of a tota	of 6 sheets, including this co	cover sheet.
	⊠	beer	n amended and are the	anied by ANNEXES, i.e. shee e basis for this report and/or s on 607 of the Administrative I	ets of the description, claims and/or drawings which have sheets containing rectifications made before this Authority Instructions under the PCT).
	Thes	e anı	nexes consist of a tota	l of 11 sheets.	
•	This	*****	t contains Indications	relating to the following items	<b>Q</b> •
3.	ins	_		relating to the lollowing hems.	
	l	$\boxtimes$	Basis of the opinion		
	II		Priority		the formation to the second for the second formation to the second formation t
	III				elty, inventive step and industrial applicability
	IV V	⊠ ⊠	Lack of unity of inve		regard to novelty, inventive step or industrial applicability;
	V		citations and explan	ations supporting such statem	ment
	VI		Certain documents	pited	
	VII		Certain defects in th	e international application	
	VIII		Certain observations	s on the international applicati	tion
Dat	e of sub	missi	on of the demand	Da	ate of completion of this report
01.	.06.20	04		10	0.03.2005
		ехап	g address of the internat lining authority:	lonal Au	authorized Officer
-		D-	ropean Patent Office 80298 Munich	C.	Catana, C
Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465			n. +49 89 2399 - 0 1X: 52 x: +49 89 2399 - 4465		elephone No. +49 89 2399-7369

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/GB 03/04665

	Basis	of	the	rep	ort
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 With regard to the elements of the international application (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)):

	Desc	cription, Pages			
1-25			as origin	ally filed	
	Clair	ms, Numbers			
	1-41		received	I on 20.10.2004 with letter of 20.10.2004	
	Drav	vings, Sheets			
	1/8-8		as origin	ally filed	
2.	With lang	regard to the langua	i <b>ge</b> , all the elemermational applic	ents marked above were available or furnished t ation was filed, unless otherwise indicated under	o this Authority in the this item.
	The	se elements were ava	ailable or furnish	ed to this Authority in the following language:	, which is:
		the language of a tra	nslation furnishe	ed for the purposes of the international search (u	nder Rule 23.1(b)).
		the language of publi	cation of the inte	ernational application (under Rule 48.3(b)).	
		the language of a tra Rule 55.2 and/or 55.3		ed for the purposes of international preliminary ex	kamination (under
3.	With inte	n regard to any <b>nucle</b> mational preliminary e	otide and/or am examination was	nino acid sequence disclosed in the international carried out on the basis of the sequence listing:	al application, the
		contained in the inter	rnational applica	tion in written form.	
		filed together with the	e international a	pplication in computer readable form.	
		furnished subsequer	itly to this Autho	rity in written form.	
		furnished subsequer	ntly to this Autho	rity in computer readable form.	
		The statement that to in the international a	he subsequently pplication as file	r furnished written sequence listing does not go b d has been furnished.	eyond the disclosure
		The statement that to listing has been furn		ecorded in computer readable form is identical to	the written sequence
4.	The	amendments have r	esulted in the ca	ancellation of:	
		the description,	pages:		
	$\boxtimes$	the claims,	Nos.:	42-52	
		the drawings,	sheets:		

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5.		This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).
		(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
6.	Add	itional observations, if necessary:
111.	Nor	n-establishment of opinion with regard to novelty, inventive step and industrial applicability
1.	The obv	questions whether the claimed invention appears to be novel, to involve an inventive step (to be non- ious), or to be industrially applicable have not been examined in respect of:
		the entire international application,
	$\boxtimes$	claims Nos. 20,36, 38-40
		because:
		the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):
		the description, claims or drawings (indicate particular elements below) or said claims Nos. are so unclear that no meaningful opinion could be formed (specify):
		the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
	⋈	no international search report has been established for the said claims Nos. 21, 22,44,46,47,50 (as originally filed)
2.	or a	neaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative tructions:
		the written form has not been furnished or does not comply with the Standard.
		the computer readable form has not been furnished or does not comply with the Standard.
I۱	/. La	ck of unity of invention
1	. In	response to the invitation to restrict or pay additional fees, the applicant has:
		restricted the claims.
		paid additional fees.
		paid additional fees under protest.
	$\boxtimes$	neither restricted nor paid additional fees.
2	. <b></b>	This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3	. Th	is Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3

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		complied with.				
		not complied with for the follow	ving re	asons:		
4.	Cor exa	nsequently, the following parts omination in establishing this rep	of the i	nternational	application were the subject of international preliminary	
		all parts.				
	$\boxtimes$	the parts relating to claims No	s. 1-19	,21-35, 37, 4	¥1.	
V.	<ol> <li>Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability citations and explanations supporting such statement</li> </ol>					
1.	Stat	tement			•	
	Nov	relty (N)	Yes: No:	Claims Claims	1-19,21-35,37,41	
	Inve	entive step (IS)	Yes: No:	Claims Claims	1-19,21-35,37,41	
	Indi	ustrial applicability (IA)	Yes: No:	Claims Claims	1-19,21-35,37,41	
2.	Cita	tions and explanations				

see separate sheet

#### INTERNATIONAL PRELIMINARY **EXAMINATION REPORT - SEPARATE SHEET**

- The subject-matter of claim 1 is directed to an oxide dispersion strengthened 1. Ni-Cr-Fe alloy as defined in claim 1 (C 0.01-0.7, Si 0.1-3, 15-90 Ni, 5-40 Cr, 0.01-4.5 Hf, balance iron and imp.), having Hf as fine oxide particles and at least one carbide forming element more stable than Cr. Nb, Ti, W, Ta and Zr.
- Reference is made to the following documents: 2.

D1: EP-A-0050408

D2: US 6409847

D3: JP-A-05001355

D4: EP-A-0391381

D5: US 5851318

- 3. Novelty
- D1 describes a Ni-Cr-Fe alloy. The composition of alloy of example C falls within the ranges as defined in claim 1 (see page 5, line 4). Alloy C contains Ti (a carbide forming element) and also 0.52 wt% Hf.

The method of producing the alloy according to the present invention is defined in claim 22. Since the method of D1 as described at page 4, line 1-12, includes the step of adding Hf before pouring as defined in claim 26, it would inevitably result in the same alloy, i.e. having at least part of Hf as oxide particles.

The subject-matter of independent claim 1 and 22 lacks novelty over the disclosure of D1 (Art. 33.2 PCT).

Following the same approach, D1 is considered as anticipating the subject-matter of claims:

2, 4, 6, 8, 10, 15, 16, 17, 21, 41 in respect of alloy;

23,29 in respect of method;

37 in respect of the tube (pipe).

- In addition, the following prior art is also considered to be novelty destroying for the cited claims:
  - 21, 41 in respect of alloy in D2 (table 1), D3 (table 1, ex. 1-4), D4 (ex. 17, table 1), D5 (table 1, ex. A-F);

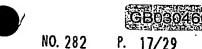
**EXAMINATION REPORT - SEPARATE SHEET** 

37 in respect of the tube (pipe) in D2 (claim 6), D3 (par. 18; abstract), D4 (page 5, line 32-34), D5 (col. 5, line 16-24).

The use of a rotational moulding to produce a tube is described i.e. in D2 (par. 16), D3 (par. 18), D4 (page 5, line 32-34).

- 3.3 The subject-matter of remaining dependent claims does not appear to add any inventive features to independent claim 1 and/or 22.
- The amendments made on 20.10.2004 to claims 20, 36, 38, 39, 40 are not allowable since they relate to unsearched matter either lacking unity (Rule 13.1 PCT) or undefined and obscure (Rule 6.2(a) PCT) as detailed in the International Search Report; the subject-matter of these claims is therefore not examined; the subjectmatter of claims 37, 41 which refers back to any of above-mentioned claims is also not to be examined. The rest of the amendments is considered to comply with Art. 19 PCT.





#### CLAIMS

1. An oxide dispersion strengthened nickel-chromiumiron alloy comprising, by weight:

5			
	Carbon	0.01 - 0.7%	
	Silicon	0.1 - 3.0%	
	Manganese	0 - 2.5등	
	Nickel	15 - 90%	
10	Chromium	5 - 40%	
	Molybdenum	0 - 3.0%	
	Niobium	0 - 2.0%	. •
	Tantalum	0 - 2.0%	
	Titanium	0 - 2.0%	
15	Zirconium	0 - 2.0%	
	Cobalt	0 - 2.0%	
	Tungsten	0 - 4.0%	
	Hafnium	0.01 - 4.5%	
	Aluminium	0 - 15%	
20	Nitrogen	0.001 - 0.5%	
	Oxygen	0.001 - 0.7%	
	balance iron	and incidental	impurities,

with the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, titanium, tungsten, tantalum and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

2. An oxide dispersion strengthened nickel-chromiumiron alloy comprising, by weight:

Carbon 0.01 to 0.5% 35 Silicon 0.01 to 2.5%



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	Manganese	0 to 2.5%
	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
5	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
10	Hafnium	0.01 to 4.5%,

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

3. An alloy according to claim 1 having the following composition, by weight:

_			
	Carbon	0.3 to 0.7%	
	Silicon	0.1 to 2.5%	
	Manganese	2.5% max.	
	Nickel	30 to 40%	
25	Chromium	20 to 30%	
	Molybdenum	3.0% max.	
	Niobium	2.0% max.	•
	Hafnium	0.01 to 4.5%	
	Titanium	0.5% max.	
30	Zirconium	0.5% max.	
	Cobalt	2.0% max.	
	Tungsten	1.0% max.	
	Nitrogen	0.001 - 0.5%	
	Oxygen	0.001 - 0.7%	
35	Balance iron an	d incidental	impurities.







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4. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.03 to 0.2%	
5	Silicon	0.1 to 0.25%	
	Manganese	2.5% max.	
	Nickel	30 to 40%	
	Chromium	20 to 30%	
	Molybdenum	3.0% max.	
10	Niobium	1.7% max.	
	Hafnium	0.01 to 4.5%	
	Titanium	0.5% max.	
	Zirçonium	0.5% max.	
	Cobalt	2.05% max.	
15	Tungsten	1.0% max.	
	Aluminium	0 - 15.0%	
. •	Nitrogen	0.001 - 0.5%	•
	Oxygen	0.001 - 0.7%	
	balance iron a	nd incidental	impurities.

5. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.7%
25	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
30	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	1.0% mak.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
35	Tungsten	1.0% max,,





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Aluminium 0 - 15.0% Nitrogen 0.001 - 0.5% Oxygen 0.001 - 0.7%

balance iron and incidental impurities.

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6. An alloy according to claim 1 having the following composition, by weight:

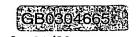
Carbon 0.03 to 0.2% 10 Silicon 0.1 to 2.5% Manganese 2.5% max. Nickel 40 to 50% Chromium 30 to 40% Molybdenum 3.0% max. 15 Niobium 2.0% max. 0.01 to 4.5% Hafnium Titanium 0.5% max. Zirconium 0.5% max. Cobalt 2.0% max. 20 Tungsten 1.0% max., Aluminium 0 - 15.0Nitrogen 0.001 - 0.5% Oxygen 0.001 - 0.7balance iron and incidental impurities.

7. An alloy according to claim I having the following composition, by weight:

Carbon 0.3 to 0,7% 30 0.01 to 2.5% Silicon Manganese 2.5% max. Nickel 19 to 22% Chromium 24 to 27% Molybdenum 3.0% max. 35 Niobium 2.0% max







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Hafnium 0.01 to 4.5%

Cobalt 2.0% max.

Tungsten 1.0% max.,

Aluminium 0 - 15.0%

Nitrogen 0.001 - 0.5%

Oxygen 0.001 - 0.7%

balance iron and incidental impurities.

8. An alloy according to claim 1 having the following 10 composition, by weight:

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max
15	Nickel	30 to 45%
	Chromium	19 to 22%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
20	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.
	Aluminium	0 - 15.0%
25	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron	and incidental impurities.

- 9. An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by weight.
  - 10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.







11. An alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

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12. An alloy according to claim 11, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

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13. An alloy according to claim 11 or 12, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

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14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

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15. An alloy according to any one of claims 1 and 4 to 8, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.

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16. An alloy according to claim 15, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.

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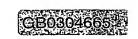
17. An alloy according to claim 15 or 16, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.



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- 18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.
- 19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.
- 20. An alloy according to any one of the preceding claims, having any one of the following compositions, by weight:

	Carbon	0.45%
	Silicon	1.3%
	Manganese	0.9%
20	Nickel	33.8%
	Chromium	25.7%
	Molybdenum	0.03%.
	Niobium	0.85%
	Hafnium	0.25%
25	Titanium	0.1%
	Zirconium	0.01%
	Cobalt	0.04号
	Tungsten	0.01%
	Nitrogen	0.1%
30	Iron	balance.
	Carbon	0.07%

1.0%

0.98%

32.5%

Silicon

Nickel

35

Manganese







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	Chromium	25.8%
	Molybdenum	0.20%
	Niobium	0.04%
	Hafnium	1.18
5	Titanium	0.12%
	Zirconium	0.01%
	Cobalt	0.04%
	Tungsten	0.08%
	Nitrogen	0.1%
10	Iron	balance.
	Carbon	0.34%
15	Silicon	1.68%
	Manganese	1.10%
	Nickel	32.0%
	Chromium	21.3%
	Molybdenum	0.018
20	Niobium	0.80%
	Hafnium	0.25₹
	Titanium	0.12%
	Zirconium	0.01%
	Aluminium	3.28%
25	Cobalt	0.04%
	Tungsten	0.01%
	Iron	balance
	Carbon	0.428
30	Silicon	1.79%
30		1.17%
	Manganese Nickel	33.2%
	Chromium	
		23.3%
	Molybdenum	0.02%

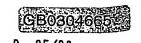
0.77%

Niobium





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	Hafnium	0.24%
	Titanium	0.10%
	Zirconium	0.01%
	Aluminium	1.64%
5	Cobalt	0.04%
	Tungsten	0.08%
	Iron	balance

- 21. An oxide dispersion strengthened nickel-chromiumiron alloy which comprises up to about 5% by weight
  of hafnium, with at least part of the hafnium being
  present as finely divided oxidised particles.
- 22. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

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- 23. A method according to claim 22, in which the alloy is an alloy as claimed in any one of claims 1 to 21.
- 24. A method according to claim 22 or 24, wherein the hafnium particles have a particle size of less than 50 microns.
- 25. A method according to any one of claims 22 to 24, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.
  - 26. A method according to any one of claims 22 to 25, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.



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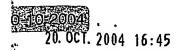




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- 27. A method according to claim 26, in which the hafnium particles are added to the molten alloy in a ladle.
- 5 28. A method according to any of claims 22 to 27, in which the hafnium is electrolytic hafnium.
- 29. A method according to any one of claims 22 to 28, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.
- 30. A method according to claim 29, in which the titanium is added in the form of TiFe after the hafnium addition.
  - 31. A method according to any of claims 22 to 30, in which the melt temperature is in the range of from 1500°C to 1700°C.
- 32. A method of manufacturing a corrosion resistant nickel-chromium-iron which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.
- 33. A method according to claim 32, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.
- 30 34. A method according to any one of claims 22 to 33, in which the alloy is formed into a tube by rotational moulding.
- 35. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium



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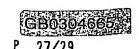
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particles to the melt before pouring.

- 36. A creep resistant alloy tube according to claim 42, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.
- 37. A tube formed from an alloy according to any one of claims 1 to 21 by rotational moulding.
- 38. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.
  - 39. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.
  - 40. A corrosion resistant tube, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to 15% of aluminium and up to about 5% of hafnium.
    - 41. An alloy according to any one of claims 1 to 21, 38 and 35 produced by a method according to any one of claims 22 to 35.